

# Comments on ‘Irreversibility in Response to Forces Acting on Graphene Sheets’

Mehdi Neek-Amal \*

Department of Physics, Shahid Rajaee University, Lavizan, Tehran 16785-136, Iran.

In Ref. [1] the compression-relaxation mechanism (CRM) for a graphene sheet (GS) was reported to be irreversible and resulted in static ripples on GS, such that for  $T < T_c$  the free-energy of the rippled GS is smaller than that of roughened GS. We will point out several technical difficulties, such as the use of the relation  $\Delta A = \langle W \rangle$  for the free energy calculations and the definition of the rough state, with their simulations [2]. We show that (at  $T < T_c$ ) their introduced rough state suffer boundary stress, thus is a rippled state and their obtained inequality  $A_{\text{ripple}} < A_{\text{rough}}$  is no longer valid. Therefore the introduced mechanism is reversible. Furthermore, from theoretical point of view for an infinitely slow rate of CRM [3], the relation  $\Delta A = \langle W \rangle$  (in common non-equilibrium simulations) is allowed [4]. In this case authors of Ref. [1] must report the used infinitely small rate and justify how it is in practice valid. We show  $\Delta A \neq \langle W \rangle$  for the system that was used in Ref. [1].

To define the rippled state it was stated in Ref. [1]: ‘we might state that any primary stress on GS, for example, in its preparation in the experiments, can construct ripples that will survive during the experimental measurements’. According to this statement, we assume that each GS (nanoribbons) with boundary stress is in the rippled state (regardless of the shape of the ripples and the other corresponding properties).

We simulated the same sample that was used in Ref. [1]. A GS with  $80 \times 40$  atoms by using the same method at  $T = 55$  K, the strain rate for CRM is  $0.0117/\text{ns}$ . The time step is  $0.5$  fs and after  $25$  ps (for thermal equilibrium, i.e. state ‘I’), we compressed the system for  $325$  ps and then relaxed it by moving back to its initial position (state ‘F’) for other  $325$  ps. Obviously this is done by applying forces on the two rows of atoms at the (longitudinal) ends. Fig. 1(a) shows 8 trajectories which are the variation of the work done on the GS versus time (8 simulations were done with different initial conditions) and the variation of  $\langle \langle h^2 \rangle \rangle$  (Fig. 1(b)). The dashed curve is  $\langle W \rangle$  which its variation is related to the dissipated work [4]. As we see (from Fig. 1(b))  $\langle \langle h^2 \rangle \rangle$  (after relaxation) decreases with time. Therefore the amplitude of the final ripples decreases after CRM. Fig. 1(c) shows the change in the free energy using Jarzynski equality (i.e.  $\Delta A = -\beta^{-1} \ln \langle \exp(-\beta W) \rangle$ ),  $\langle W \rangle$  and  $\Delta A - \langle W \rangle (= -0.5\beta\sigma_w^2)$  and clearly  $\Delta A \neq \langle W \rangle$ . The difference  $\Delta A - \langle W \rangle$  is just the dissipated work which is associated with the increase of entropy [3, 4]. Practically, the latter difference must be considered even by very small rate of

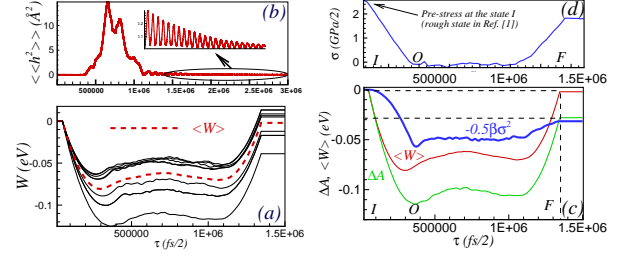


FIG. 1: (Color online) (a) Variation of the total works for 8 different trajectories (solid curves) and the average work (dashed curve), (b)  $\langle \langle h^2 \rangle \rangle$  vs time (inset is zoomed region after relaxation), (c) free energy change, the average work and dissipated work and (d) boundary stress during CRM.

CRM which is in contrast to the assumption  $\Delta A = \langle W \rangle$  in Ref. [1].

The size of the system at state ‘I’ is assumed to be equal to a flat GS (it is due to performing NVT ensemble in Ref. [1]) for a sample size with  $80 \times 40$  atoms (‘rough state’ in Ref. [1]). Fig. 1(d) shows the variation of (absolute value of) boundary force per width (i.e. stress) versus CRM time (the averaged value over 8 simulations). As we see from the top panel in Fig. 1(d) at state ‘I’ (‘rough state’ in Ref. [1]) the system is not free from stress and it feels pre-stress around 4 GPa which is not negligible [5] (the reason is that the GS does not have the optimum size [6] at ‘I’). Here we emphasize that the behavior of boundary stress around points ‘I’ (and ‘F’) is always similar to that one we presented here. After some compression steps the free energy curve shows the first minimum, i.e. state ‘O’. At this state the system is almost free of boundary stress (Fig. 1(d)). Moving back to the initial position by stretching the system, after passing another minimum [7] we obtain the state ‘F’, which is not free from boundary stress too (‘ripple state’ in Ref. [1]). Therefore both the initial and final state in CRM are rippled states [6]. Moreover, the state ‘O’ should be considered as the true ‘rough state’ in Ref. [1], where there is no boundary stress and the relation  $A_O - A_F < 0$  holds [6]. The latter inequality implies that the state ‘O’ is much stable than the rippled states ‘F’ and ‘I’. In Ref. [1] the inequality  $A_F - A_I$  is referred to as the difference between rippled (with stress) and the rough state (without stress) i.e. difference between two dashed horizontal lines in Fig. 1(c), however we see that this is only the difference between two rippled states, i.e. ‘I’ and ‘F’. The final remark is that in Ref. [1], there is no physical reason given for the irreversibility except that  $A_F - A_I < 0$ , which we have shown this is not valid.

\*neekamal@srttu.edu

Note that the existence of the boundary stresses at the states ‘ $I$ ’ and ‘ $F$ ’ are independent of other parameters (e.g. rate for CRM, amount of compression, size of the system and temperature [8]).

In summary, the true ‘*rough state*’ has lower free en-

ergy with respect to the rippled state. Using the Jarzynski equality is necessary when calculating the free energy change in the CRM of GS even for very slow evolution. Both initial and final states in the simulations of Ref. [1] are rippled states thus the CRM is reversible.

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- [1] N. Abedpour, Reza Asgari, and M. Reza Rahimi Tabar, Phys. Rev. Lett **104**, 196804 (2010).
- [2] Some other errors are:
1. The quantity  $\langle |h_q|^2 \rangle$  in Fig. 1 is shown in  $\text{\AA}^2$  unit, which is in contrast to the given formula  $\langle |h_q|^2 \rangle = \frac{N K_B T}{k q^4}$  where indicates the  $\text{\AA}^4$  unit.
  2. One can simply estimate the bending rigidity from (linear part of) Fig. 1 to  $\sim 330067$  eV where  $L = 852$   $\text{\AA}$ , surprisingly, it is by five orders of magnitude higher than the reported value (1.0 eV) in the text. This large number is meaningless.
  3. The bending rigidity has eV unit not  $\text{eV}^{-1}$ .
  4. In Fig. 1  $\langle |h_q|^2 \rangle$  is plotted versus  $|\mathbf{q}|/q_0$  not  $\mathbf{q}/q_0$  as mentioned in the caption. This may affects the figure’s message seriously.
  5. Proposed formula  $(\lambda(50) \simeq 35 \ln(50) - 55)$  gives the value 81.9  $\text{\AA}$  for ripple’s wave length, different from reported value 85  $\text{\AA}$ .
  6. To support validity of the results, one naturally expects that the internal energy and the entropy for  $T = 40$  K and 150 K are presented in Fig. 2, especially, when they are simply reported by the code.
  7. The same problem for free energy and entropy at 85 K (in Fig. 2). Moreover, 90 K is an important threshold (for conclusion) in Ref. [1], but neither free energy nor entropy are not presented for this temperature (Fig. 2)
- [3] H. Xiong, A. Crespo, M. Marti, D. Estrin, and A. E. Roitberg, Theor. Chem. Acc. **116**, 338 (2002).
- [4] C. Jarzynski, Phys. Rev. Lett **78**, 2690 (1997).
- [5] C. Lee, X. Wei, J. W. Kysar, and J. Hone, Science **321**, 385 (2008).
- [6] The rough state in Ref. [1] and the given comparison for the ripple wave lengths with other literature is wrong. The ripple wave length in Ref. [1] have compared to the one reported by A. Fasolino *et al* [9]. In Ref. [9], GS were equilibrated for 400,000 MC steps (having NPT ensemble) to make the system relaxed (zero pressure) and then they found ripples even at 3500 K. Therefore, 1) the assumption of the rough state in Ref. [1] is similar to the meaning of ripples in Ref. [9] (no stress exists) and 2) if the meaning of the ripples in Ref. [1] and ref [9] are the same (as assumed in Ref. [1]) one found ripples in 3500 K (Ref. [9]) and one claims that there is no ripples after relaxation of the system above 100 K [1]. Thus, it is wrong and confusing to compare ripple structure in Ref. [1] to the one found in Ref. [9].
- By performing an NPT ensemble in MC (or MD) simulation with periodic boundary condition, one can find the real equilibrium state (out of stress) as well as done by K. V. Zakharchenko *et al* in Phys. Rev. Lett. **102**, 046808 (2009); or by H. Zaho *et al* in Nano. Lett. **9**, 3012 (2009). Nevertheless, neglecting this conceptual difficulties, we showed that the CRM is reversible.
- [7] The smaller strain rate yields similar two minima.
- [8] We performed another simulation with smaller rate (0.0064/ns), the smoother curves in Fig. 1 was found, but the overall behavior is the same.
- [9] A. Fasolino *et al* in Nature Mater. **6**, 858 (2007).